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Brightness Reversion of Mechanical Pulps XVI: The Effect of Oxygen on  
Photostabilization of High-Yield Mechanical Pulps by UV Absorbers  
and Fluorescence Whitening Agent

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**BRIGHTNESS REVERSION OF MECHANICAL PULPS XVI:  
THE EFFECT OF OXYGEN ON PHOTOSTABILIZATION OF HIGH-YIELD  
MECHANICAL PULPS BY UV ABSORBERS AND FLUORESCENCE  
WHITENING AGENT**

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**ABSTRACT**

The brightness reversion of softwood (SW) and hardwood (HW) bleached chemi-thermomechanical pulps (BCTMP) under argon, oxygen, and air has been studied in the absence and presence of several UV absorbers or fluorescent whitening agent (FWA-1). TAPPI brightness as a function of photolysis time indicates that photoyellowing of mechanical pulps occurs not only in the presence of oxygen and air but also in the presence of argon. Photoyellowing was found to be more significant for SW than for HW BCTMP testsheets. In the presence of 2,4-dihydroxy-benzophenone (DHB) and hydroxy-phenylbenzotriazole (HPB), the photoaging process is very similar for HW BCTMP handsheets under an argon or air atmosphere. Irradiation in a pure oxygen atmosphere causes a significant loss of brightness. Substantial differences in photoaging for the additive-treated SW BCTMP testsheets were observed under all three atmospheres. Brightness reversion of SW and HW BCTMP handsheets treated with FWA-1 were significantly impacted when the photolysis experiments were performed in an oxygen

atmosphere. These results are supportive of a multi-reaction pathway leading to the photodiscoloration of high brightness mechanical pulps.

### **Application**

The application of UV absorbers or a fluorescent whitening agent can significantly reduce brightness reversion of high brightness mechanical pulps. Photoyellowing of additive-treated BCTMP handsheets in an inert atmosphere, such as argon, suggests that brightness reversion is a multi-faceted process that will require an additive mixture to retard photoyellowing.

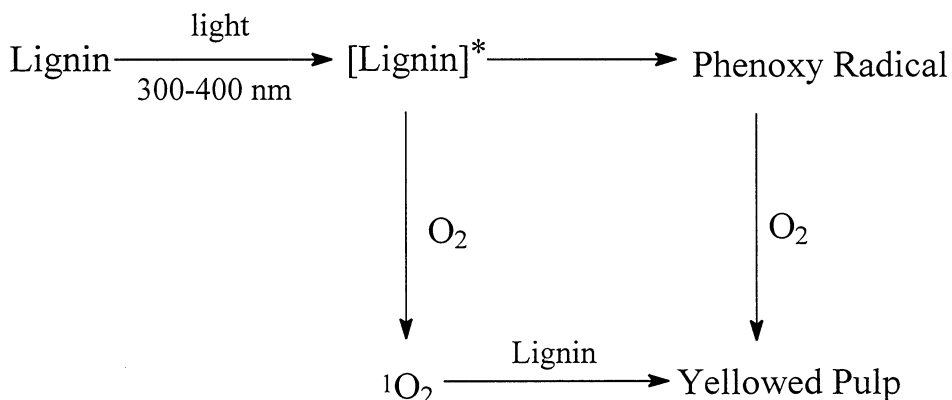
### **KEYWORDS**

Brightness reversion, photostabilization, oxygen effect, UV absorber, fluorescent whitening agent

### **INTRODUCTION**

The commonly accepted mechanisms for brightness reversion involve the absorption of a photon of the UV light by extended conjugated structures present in lignin, such as  $\alpha$ -carbonyl groups or olefinic structures with a phenyl ring.<sup>1</sup> The excited states of these compounds can undergo a series of chemical reactions ultimately resulting in the photodiscoloration of mechanical pulps. Oxygen is frequently proposed to be a key component of the photoyellowing process either by trapping reactive lignin radicals or by the formation of singlet oxygen.<sup>2</sup> Singlet oxygen has been proposed to further undergo the charge transfer reactions with lignin to form a variety of radical intermediates.<sup>2-6</sup> Scheme 1 summarizes the proposed role of molecular oxygen in brightness reversion.

### SCHEME 1



A direct means of evaluating the role of molecular oxygen on brightness reversion of high yield pulps is to study the photoreversion properties of mechanical pulp under differing atmospheres. Indeed, early studies by Van der Akker et al.<sup>7</sup> reported that light-induced yellowing of groundwood pulp was retarded when irradiated in a nitrogen (N<sub>2</sub>) atmosphere. Leary<sup>8</sup> has also shown that newsprint will not undergo brightness reversion when irradiated in an N<sub>2</sub>, CO<sub>2</sub>, or vacuum atmosphere. Lin and Kringstad<sup>9</sup> have shown that milled wood lignin photolyzed in a methylcellulose-water mixture did not discolor when irradiated under vacuum, whereas in the presence of air the irradiation solution rapidly discolored. Recent studies by Destine et al.<sup>10</sup> have shown that the molecular weight of milled wood lignin photolyzed in a solution of dioxane-water changes dramatically, depending on the presence or absence of oxygen. These results were attributed to the unique capabilities of oxygen trapping reactive lignin radicals formed during irradiation.

It is well known that UV-absorbing additives can retard the overall rates of brightness reversion. Some of the most effective additives are derived from benzophenone, benzotriazole, or diamino-stilbene structures.<sup>11-15</sup> To further explore the chemistry involved in retarding brightness reversion of BCTMP pulps, we examined the

photoyellowing properties of SW and HW BCTMP handsheets treated with 2,4-dihydroxybenzophenone (DHB), hydroxy-phenylbenzotriazole (HPB), or 2,2'-(1,2-ethenediylbis(3-sulfo-4,1-phenylene)imino(6-di-ethylamino)-1,3,5-triazine-1,2-diyl(imino))bis-1,4-benzene-disulfonic acid, hexasodium salt (FWA-1) (see Figure 1) irradiated in an atmosphere of argon, air, or oxygen.

## EXPERIMENTAL

### Materials

All chemicals and reagents including 2,4-dihydroxybenzophenone (DHB), 2-[2-hydroxy-3-*t*-butyl-5-(2-octyloxycarbonyl)ethyl-phenyl]2H-benzotriazole (HPB), and 2,2'-(1,2-ethenediylbis(3-sulfo-4,1-phenylene)imino(6-diethylamino)-1,3,5-triazine-1,2-diyl(imino))bis-1,4-benzene-disulfonic acid, hexasodium salt (FWA-1) were commercially purchased and used as received. Commercial HW and SW BCTMP were employed for all studies. The pulps were manufactured employing hydrogen peroxide for the chemical impregnation and bleaching stages. Compressed argon, oxygen, and air were purchased from Air Products and used as received.

### Instrumentation

A Technidyne Brightimeter Micro S-5 was employed to measure the TAPPI brightness of handsheets in terms of TAPPI procedure T452 om-92.<sup>16</sup> The photoaging experiments were performed on a Rayonet Photochemical Reactor (RPR-100) with 4 black lamps, which have a Gaussian spectral distribution between 300 and 400 nm and maximum output at ~350 nm.

### Procedures

*Preparation of pulps and testsheets.* The SW and HW BCTMP pulps were Soxhlet extracted with acetone for 24 hours and air-dried prior to testsheet formation. Testsheets (156 g/m<sup>2</sup>) were prepared following TAPPI standard procedure T 205 om-88<sup>16</sup> and air dried at constant temperature (22.0 ± 2.0°C) and relative humidity (50 ± 2.0%). The TAPPI brightness values<sup>16</sup> for the SW and HW BCTMP testsheets were 78.9 and 83.4, respectively.

*Testsheets treated with additives.* In a typical experiment, a BCTMP testsheet was sprayed with a methanolic solution (10 mL) of the additives (0.047 mmol/g of paper, *ca.* wt. 1%) and then allowed to air-dry overnight in the absence of light. Control testsheets were prepared in an analogous manner except that the UV absorber was omitted from the methanol solution.

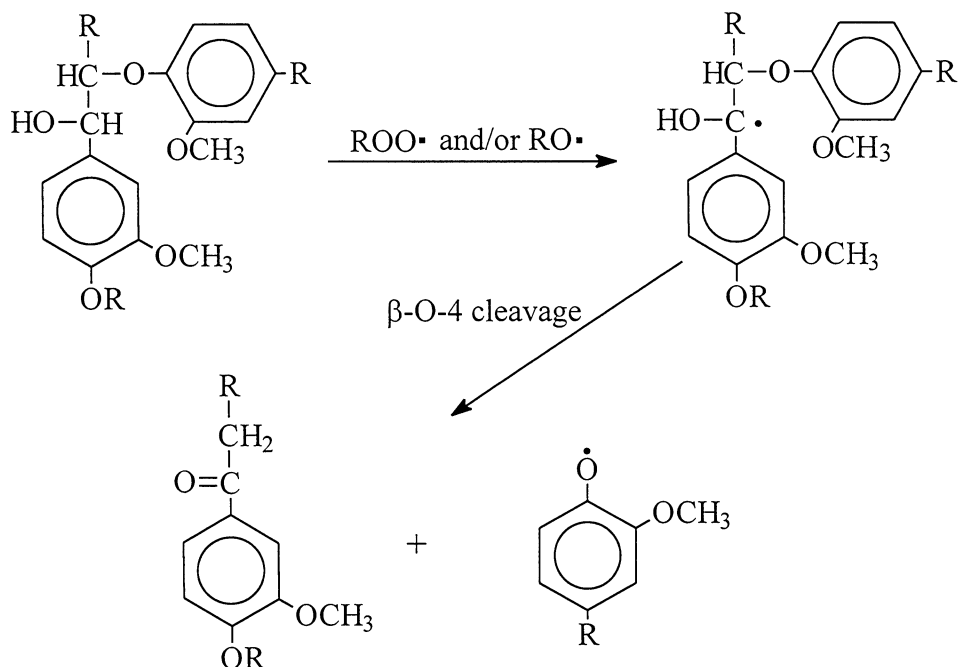
*UV photolysis of paper samples.* The treated and untreated testsheets were cut into strips ( $3 \times 7$  cm). The strips were put into a quartz sample chamber (diameter: 4.5 cm; length: 18 cm) sealed with an O-ring vacuum adapter. The samples were evacuated ( $\sim 0.02$  Torr) for 60 min, were then purged with the appropriate gas for 20 min, then evacuated 15 min and then purged for 30 min with the appropriate gas. The sample chamber was placed in the center of a merry-go-round and photolyzed in a Rayonet RPR-100 photochemical reactor with four black lamps at  $\sim 30^\circ\text{C}$ . At selected time periods, the testsheets were removed from the reactor and kept in the dark for 2 hours to equilibrate to constant temperature ( $22.0 \pm 2.0^\circ\text{C}$ ) and relative humidity ( $50 \pm 2.0\%$ ). TAPPI brightness of testsheets was measured as a function of photolysis time.

## RESULTS AND DISCUSSION

### Effect of Argon, Oxygen, and Air on Brightness Reversion of BCTMP

The photoaging properties of SW and HW BCTMP testsheets, as a function of photolysis time, under an atmosphere of argon, oxygen, or air, are shown in Figure 2. In general, the rate of brightness reversion is slower for HW handsheets than for SW BCTMP testsheets. These differences in reversion rates can be attributed to the difference in lignin content and structure.<sup>17</sup> In general, the testsheets irradiated in argon suffered the least loss of brightness. The presence of argon was shown to stabilize the slow phase of brightness reversion. The rate of brightness loss in the presence of oxygen was found to be greater than in air, but, interestingly, it was not proportional to the increase in oxygen content. Based on literature results, the photoyellowing of mechanical pulp under air and oxygen can be attributed principally to the "ketyl" pathway (see Scheme 2).<sup>18</sup>

## SCHEME 2



Inasmuch as no oxygen is present in the argon photolysis studies, no peroxy ( $\text{ROO}\cdot$ ) radicals or singlet oxygen could be formed and hence the proposed "ketyl" pathway for photoyellowing should be significantly inhibited. As a result, the observed brightness reversion under an argon atmosphere, which is much different compared to that under air and oxygen, needs to be attributed to alternative photoyellowing mechanism(s). According to literature results, the photoformation of free phenoxy radical and/or phenacyl decomposition is a likely possibility.<sup>2,19</sup>

The photoyellowing properties of SW and HW BCTMP testsheets in an inert atmosphere were further explored by performing analogous irradiation under vacuum. The behavior of brightness reversion is very similar to an argon atmosphere. Figure 3 summarizes the results of these studies. These latter studies support the hypothesis that BCTMP testsheets are prone to photodiscoloration, even in the absence of oxygen, suggesting that several photoaging mechanisms are available to irradiated BCTMP in



addition to the "ketyl" pathway. The "phenoxy radicals" and "phenacyl" pathways could readily account for these reversion results.<sup>19</sup>

Destine *et al.*<sup>18</sup> reported that photolysis of dioxane solutions of milled-wood lignin under nitrogen and oxygen cause the formation of both low and high molecular weight photoproducts under nitrogen. In contrast, under an oxygen atmosphere, the formation of low molecular weight photoproducts was shown to be predominant. They suggested that in the presence of oxygen, the carbon-centered radicals form peroxy radicals that do not condense to higher molecular weight products. Our studies are consistent with these results, in that we, too, observe photoreversion chemistry occurring both in the presence and absence of oxygen.

#### **Effect of Additives on Brightness Reversion under Argon, Oxygen, and Air**

The use of UV additives, such as DHB, HPB, or FWA-1 to significantly retard the overall rates of photoyellowing of mechanical pulp has developed rapidly over the last decade.<sup>11,13</sup> To study the overall interactions among UV screens, pulp, and oxygen, a series of treated handsheets were irradiated in either an argon, oxygen, or air atmosphere and their optical properties were evaluated.

Figures 4-7 summarize the overall rates of brightness reversion of HW and SW BCTMP handsheets in the presence of UV additives in argon, air, and oxygen atmospheres. The presence of the additives results in a significant reduction in photoyellowing of HW and SW BCTMP testsheets under the three different atmospheres studied, especially in the slow phase of brightness reversion. In all cases, the presence of oxygen increased the overall rates of brightness reversion. HW BCTMP handsheets treated with either DHB or HPB exhibited only minor differences in photoyellowing when the atmosphere was changed from argon to air to oxygen. This result suggests that the photochemistry involved in chromophore formation of additive-treated handsheets is not solely related to the formation of singlet oxygen and/or oxygen-trapped radicals. The photoreversion of SW BCTMP handsheets treated with DHB or HPB, however, are more sensitive to the presence of oxygen, which is shown to be most detrimental to the slow phase of brightness reversion of SW BCTMP handsheets. The results suggest that

different photochemical pathways are involved in brightness reversion of this furnish, potentially involving oxygen-trapped radicals.

As shown in Figures 8-9, the SW and HW BCTMP handsheets treated with FWA-1 exhibited pronounced differences in brightness reversion, depending on the atmosphere employed. With increasing oxygen content in the irradiating atmosphere, the observed photoreversion properties dramatically increased. Indeed, in 100% oxygen, the rates of brightness reversion were higher than those of the untreated sheets. This observation suggests that the oxygen could quench the excited state of FWA-1 and lead to fast formation of chromophores.

The presence of oxygen was shown to be most detrimental to the slow phase of brightness reversion. As can be seen from Figure 8, the photostabilization of HW BCTMP by FWA-1 in the presence of oxygen is eliminated after four-hour photolysis. The rate of brightness loss under 100% oxygen is much faster than that in the presence of DHB and HPB. The absence of oxygen can also result in the brightness reversion, whereas the presence of oxygen can increase the rate of brightness reversion, suggesting that the reactions can lead to the formation of the same and/or very similar products. The results may also suggest that the secondary chromophores undergo further reactions in the presence of FWA-1.

## CONCLUSIONS

The effect of oxygen on brightness reversion is more significant for SW BCTMP than it is for HW furnish. Nonetheless, SW and HW BCTMP furnishes suffered from photodiscoloration when irradiated in vacuum or under an inert atmosphere of argon. These results differ from the early studies reported by Leary on photoreversion of newsprint in CO<sub>2</sub> which did not undergo photoyellowing. These differences, undoubtedly, are due to the differences in the nature of the lignin in these different high yield pulps. One of the most commonly attributed chromophores involved in the photodiscoloration of high-yield pulps is *ortho*- and *para*-quinones. These structures can be produced, in part, via phenoxy and phenacyl radicals under an argon atmosphere. Our results are consistent with

the suggestion by Schmidt that the formation of quinone chromophores is dependent on oxygen and through the reactions of the breakdown of  $\beta$ -O-aryl ethers.

The presence of the three additives studied in this report demonstrates that they can retard photoyellowing. The previously unreported sensitivity of these additives to oxygen suggests that the additives influence different parts of the overall brightness reversion process. It is interesting to note that all three additives are most effective in the slow phase of brightness reversion, suggesting the need for alternate additives for the fast phase of brightness reversion.

## ACKNOWLEDGMENTS

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## FIGURE CAPTIONS

Fig. 1. The chemical structures of UV absorbers and fluorescent whitening agent.

Fig. 2. Brightness reversion of SW and HW BCTMP as a function of photolysis time under argon, air, and oxygen.

Fig. 3. Brightness reversion of SW and HW BCTMP as a function of photolysis time under vacuum.

Fig. 4. Brightness reversion of HW BCTMP in the presence of DHB as a function of photolysis time under argon, air, and oxygen (Control is HW untreated sheet under argon).

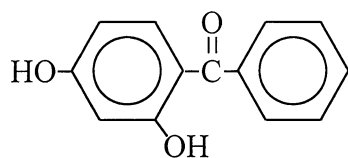
Fig. 5. Brightness reversion of SW BCTMP in the presence of DHB as a function of photolysis time under argon, air, and oxygen (Control is SW untreated sheet under argon).

Fig. 6. Brightness reversion of HW BCTMP in the presence of HPB as a function of photolysis time under argon, air, and oxygen (Control is HW untreated sheet under argon).

Fig. 7. Brightness reversion of SW BCTMP in the presence of HPB as a function of photolysis time under argon, air, and oxygen (Control is SW untreated sheet under argon).

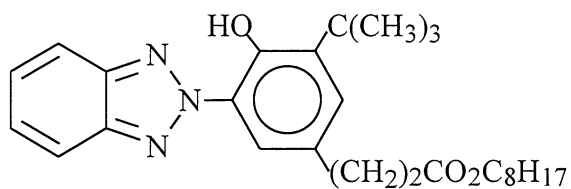
Fig. 8. Brightness reversion of HW BCTMP in the presence of FWA as a function of photolysis time under argon, air, and oxygen (Control is HW untreated sheet under argon).

Fig. 9. Brightness reversion of SW BCTMP in the presence of FWA as a function of photolysis time under argon, air, and oxygen (Control is SW untreated sheet under argon).



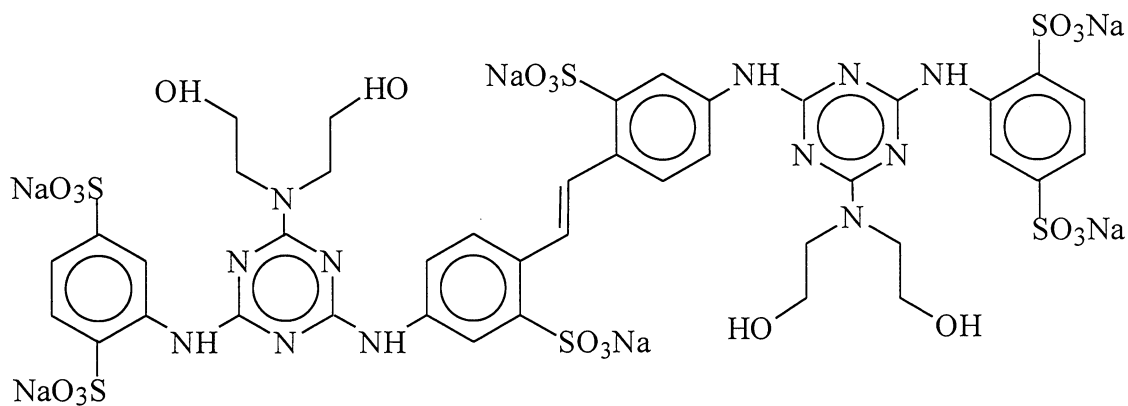
**DHB**

2,4-dihydroxybenzophenone



**HPB**

2-[2-hydroxy-3-*t*-butyl-5-(2-octyloxycarbonyl)-ethyl-phenyl]2H-benzotriazole



**FWA-1**

2,2'-(1,2-ethenediylbis(3-sulfo-4,1-phenylene)imino(6-diethylamino)-1,3,5-triazine-1,2-diyl(imino))bis-1,4-benzene-disulfonic acid, hexasodium salt

Figure 1

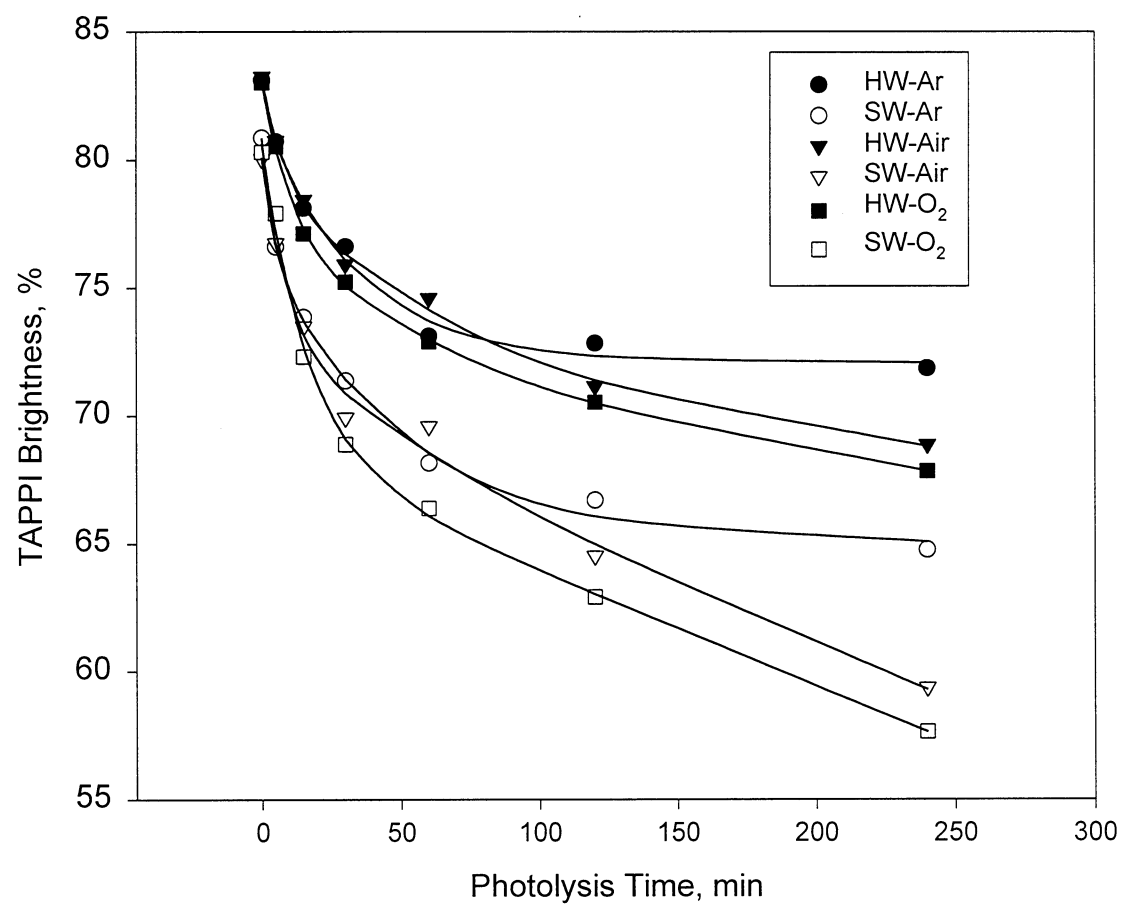


Figure 2

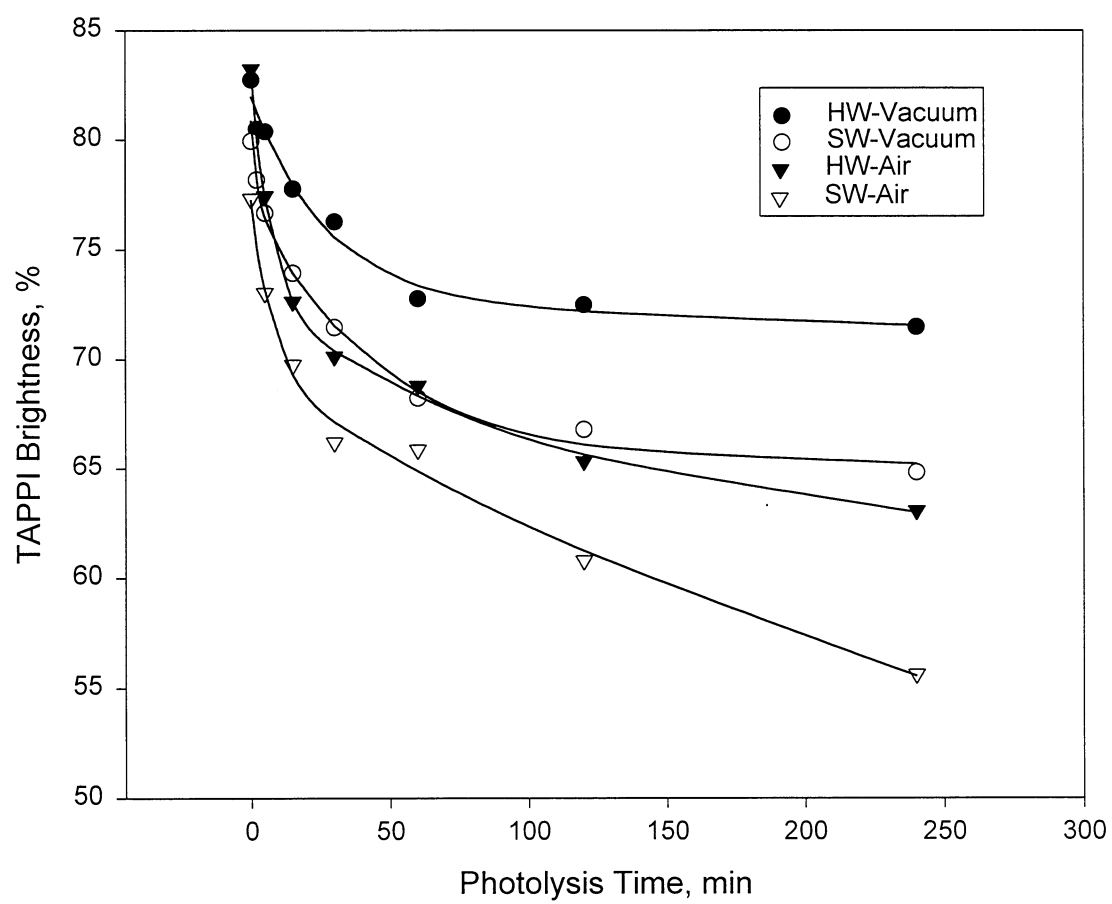


Figure 3



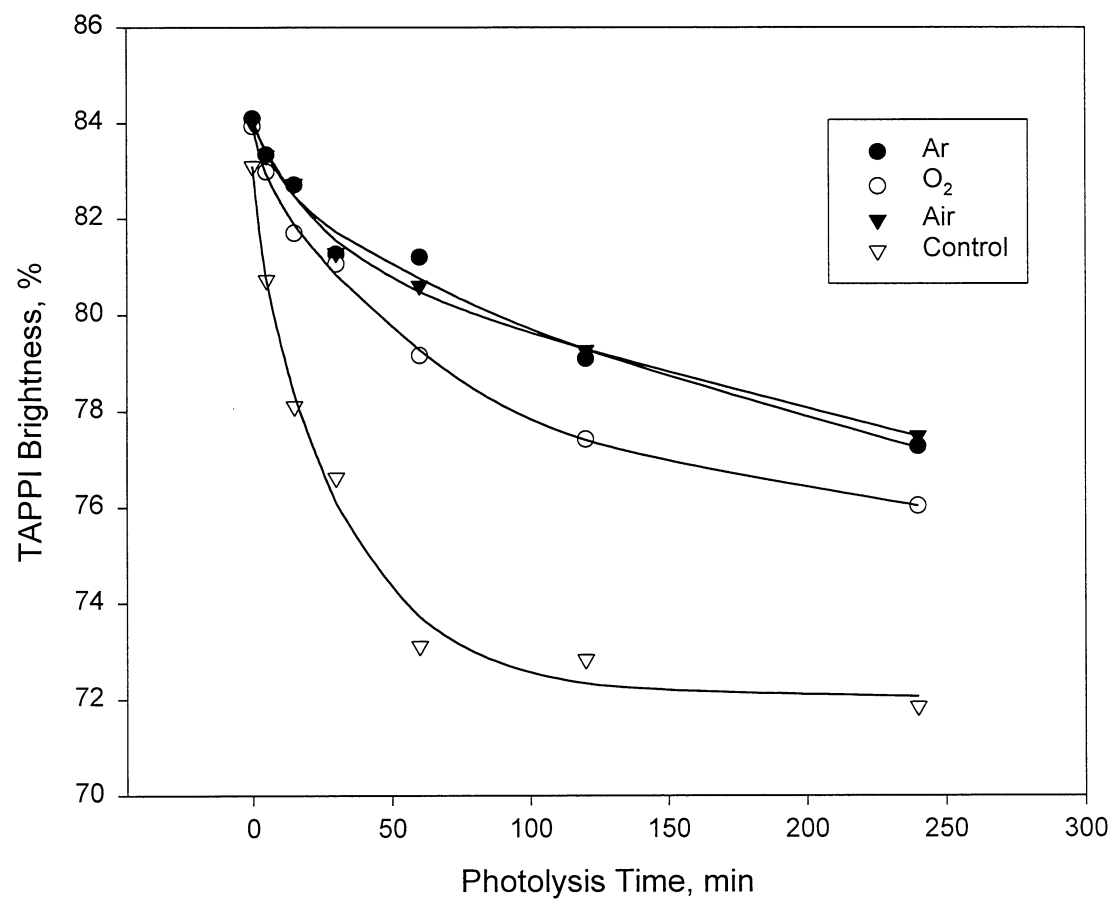


Figure 4

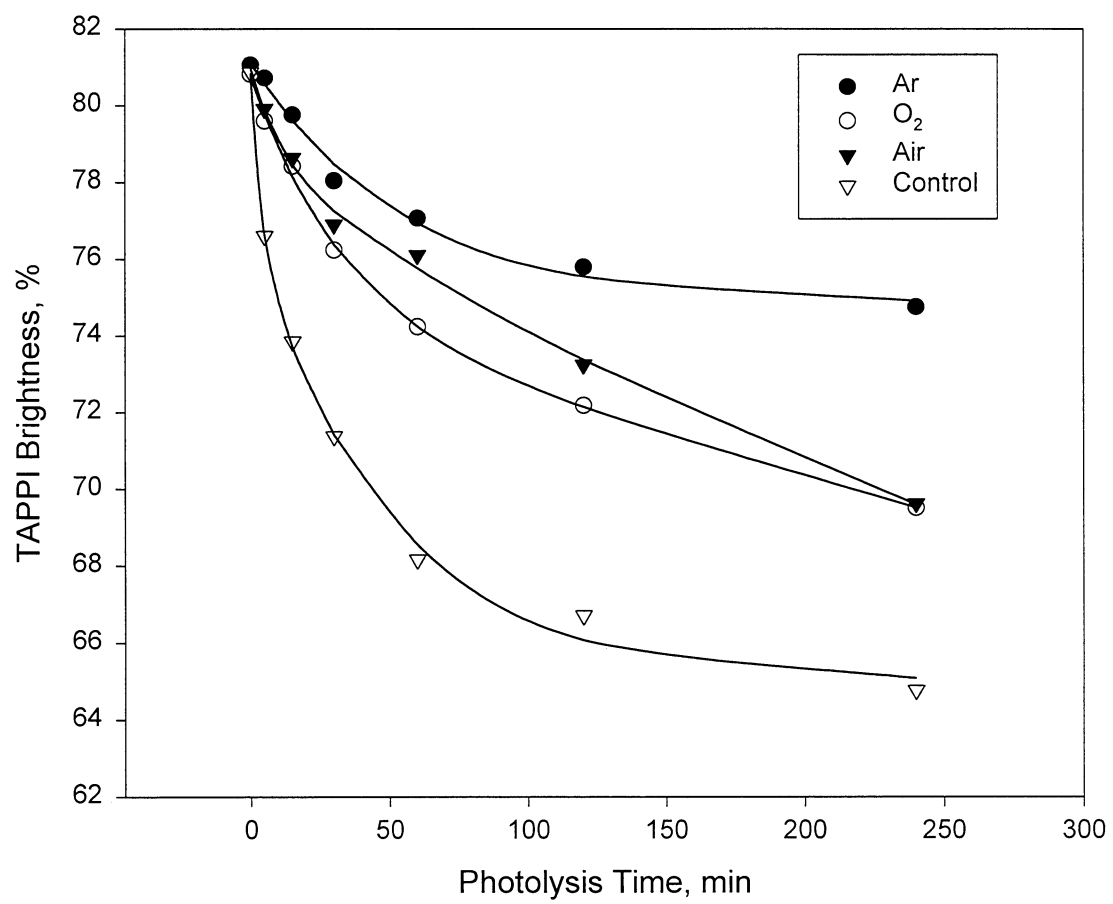


Figure 5

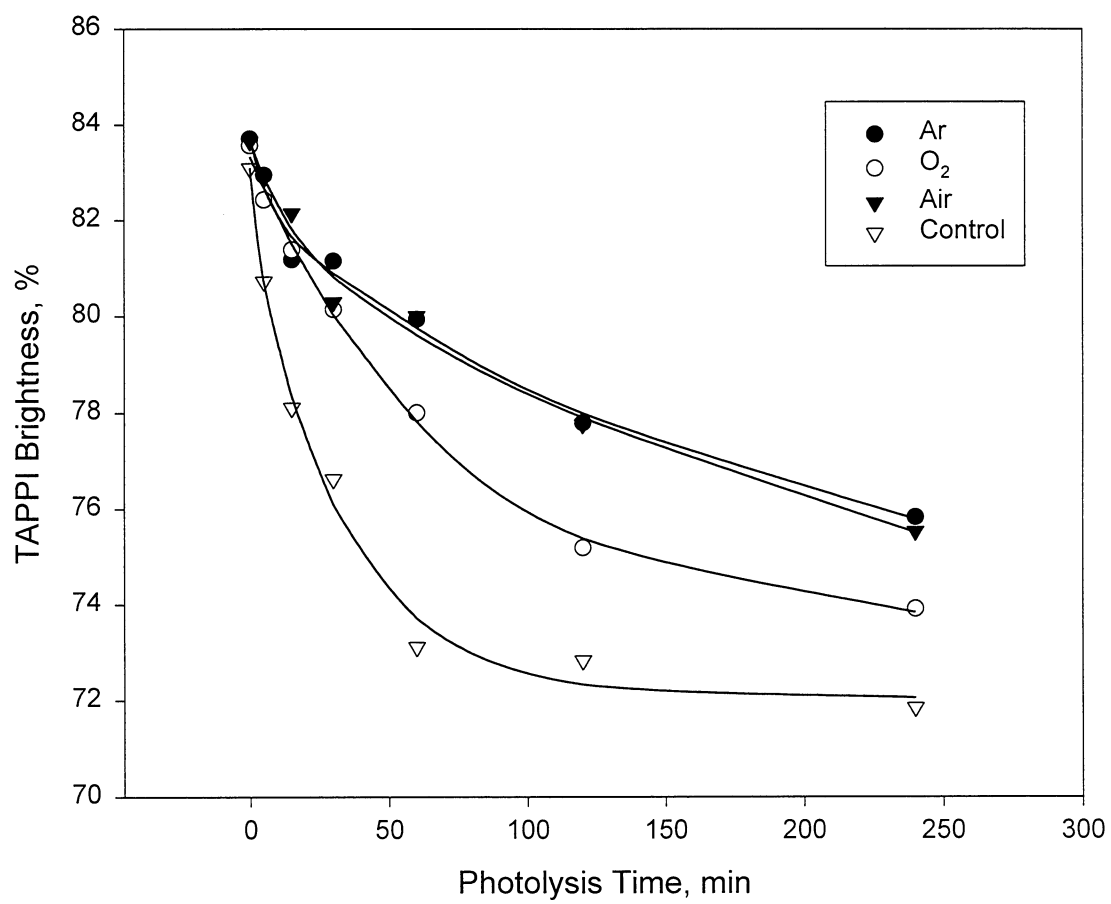


Figure 6

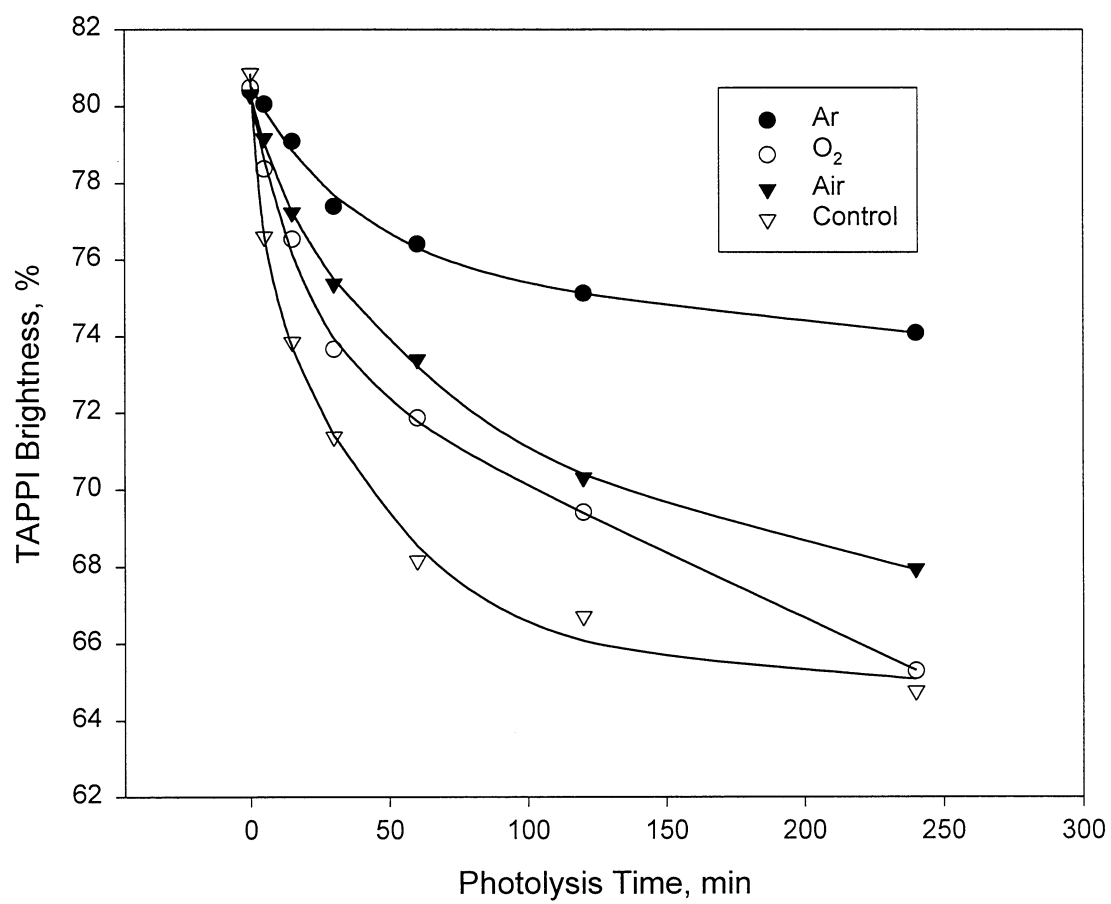


Figure 7

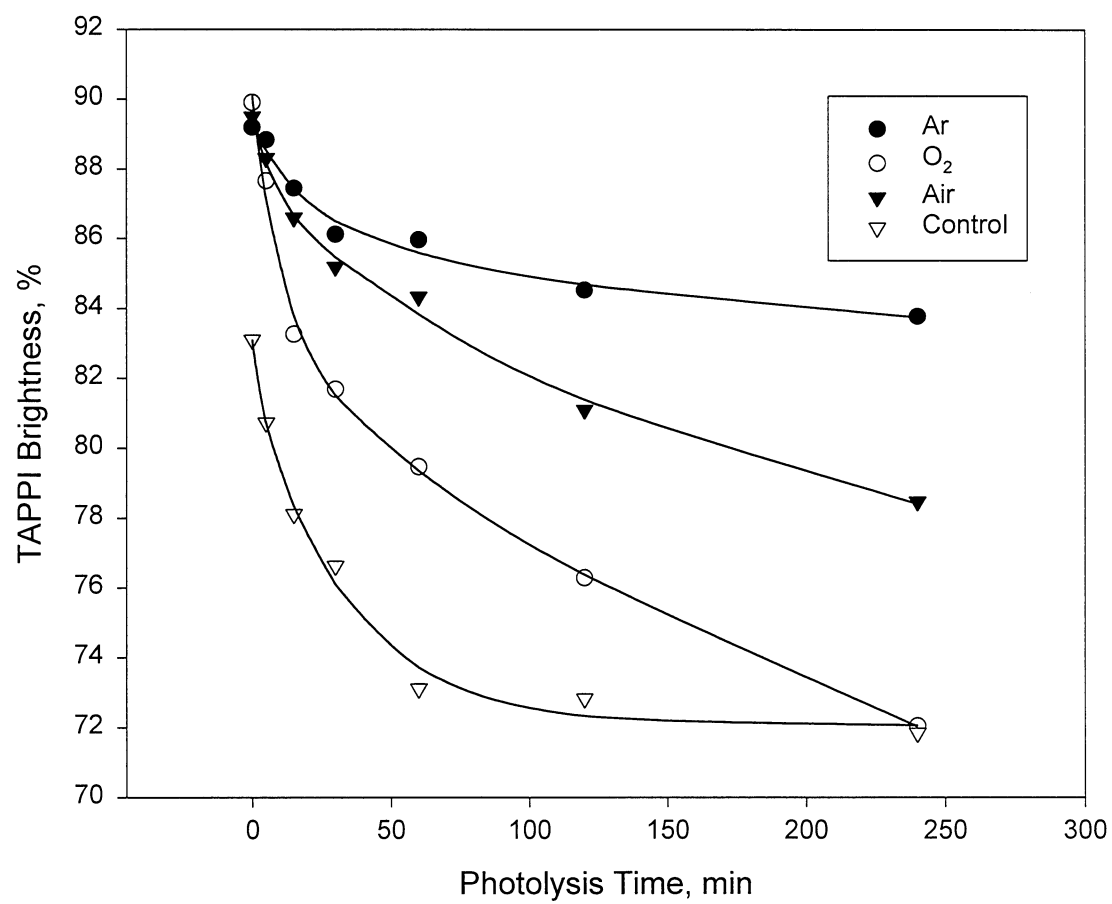


Figure 8

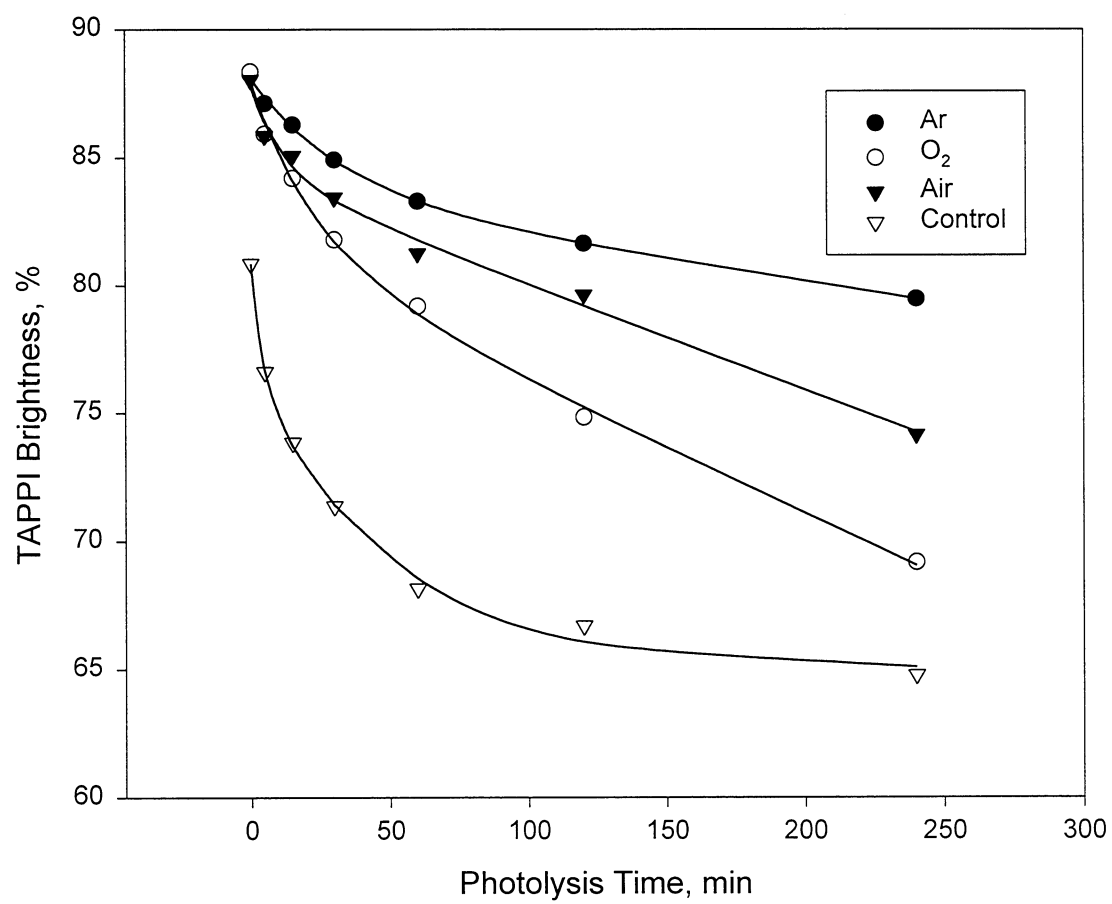


Figure 9

